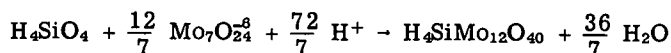


The Degrees of Anion Condensation in Silicic Acids and Silicates

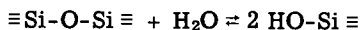
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The silicate is transformed by treatment with methanolic HCl into the free silicic acid corresponding to the anion which it contains. In favorable cases, the degree of condensation of the dissolved silicic acid can be determined by a kinetic method based on the rate of formation of the molybdosilicic acid complex. Where a complex distribution of anion sizes exists, e.g., in calcium silicate hydrate gels, the method does not give absolute results, though it can be used to follow changes in this distribution.

•ON ADDING an acidified solution of paramolybdate to a solution of monomeric silicic acid (H_4SiO_4), the molybdosilicic acid complex is formed directly according to the reaction



Condensed silicic acids also yield the same molybdate complex (1). This is because the paramolybdate solution causes Si-O-Si bonds to hydrolyze more quickly than they are formed by condensation. This equilibrium reaction corresponds to the scheme



From the results of some recent investigations it can be assumed that the rate of formation of the molybdate complex depends on the degree of condensation of the silicic acid in solution. The present method is also based on the fact that the time needed for the hydrolytic degradation increases with the degree of condensation, i.e., with the number of Si-O-Si bonds that must be hydrolyzed.

The relation between the degree of condensation and the rate of complexing applies only to silicic acids in solution. It can nevertheless also be used to estimate the degree of condensation of the anion in a silicate, provided that the free silicate with an acid present in a suitable solvent readily dissolves in this solvent. Alexander (2), O'Connor (3) and Weitz, Franch and Giller (4) studied two silicic acids which they brought into solution in different ways, while Frydrych (5) and Thilo, Wieker and Stade (6) estimated the complexing rates of three different silicic acids. We attempt here to discuss the reaction kinetics for five different silicic acids.

In order to obtain defined and uniform silicic acids in solution it is strictly necessary that a silicate, the structure of which is already known, be dissolved within one minute.

EXPERIMENTAL PROCEDURE

Solutions Required

Besides methanol, the following aqueous solutions of analytical purity will be needed:

1. 32 percent hydrochloric acid ($d = 1.156$);
2. Quinoline solution: 20 ml quinoline are poured into 900 ml water, 25 ml HCl (1) added, and the mixture diluted with water to 1000 ml;

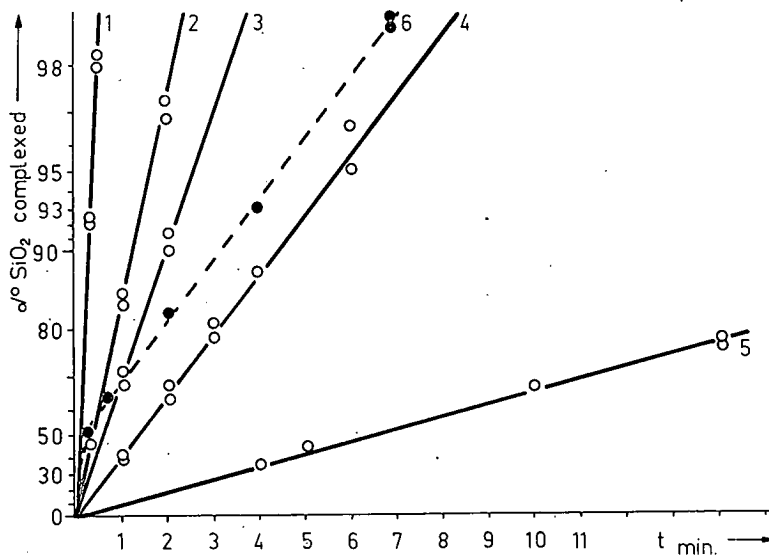


Figure 1. Kinetics of the complexing reaction for silicic acids of known degrees of condensation (% SiO_2 complexed on log scale): 1—monosilicic acid, H_4SiO_4 ; 2—disilicic acid, $\text{H}_6\text{Si}_2\text{O}_7$; 3—trisilicic acid (rings), $\text{H}_8\text{Si}_3\text{O}_9$; 4—tetrametasilicic acid (rings), $\text{H}_8\text{Si}_4\text{O}_{12}$; 5—hexametasilicic acid (rings), $\text{H}_{12}\text{Si}_6\text{O}_{18}$; 6—mixture of 4 mol H_4SiO_4 and 1 mol $\text{H}_8\text{Si}_4\text{O}_{12}$.

3. Mixed indicator: 0.1 g Cresol Red and 5.3 ml 0.1 N NaOH dissolved in water and diluted to 100 ml, 0.1 g Thymol Blue dissolved in 20 ml ethanol, 2.1 ml 0.1 N NaOH added, diluted with water to 100 ml and then mixed with the Cresol Red solution;

4. 0.5 N hydrochloric acid solution;

5. 1 N sodium hydroxide solution;

6. Molybdate solution: 70 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ dissolved in 900 ml water and then diluted to 1000 ml; and

7. Acidified molybdate solution as complexing reagent (this solution does not keep and must be prepared freshly each day): 30 ml molybdate solution (6) + 8.4 ml (4) + 1.6 ml H_2O (diluted to 40 ml).

It is necessary to have a thermostat maintained at 20 C (± 1 deg).

Preparation of the Silicate Solution

A beaker (250 ml) is placed in the thermostat so that it reaches a temperature of 20 C and 9 ml of methanolic HCl are then added. The silicate is finely powdered and sieved (particle size $< 20 \mu$), and is then weighed into a small crucible with a volume of 2-5 ml. The amount taken must be such as to contain 10 mg of SiO_2 . Methanol (1 ml) is added and the powder is dispersed by stirring with a glass rod. The crucible is then placed in the beaker containing 9 ml of methanolic HCl. The silicate powder must be thoroughly dispersed in the methanol by shaking and stirring while dissolving.

Two points must be noted. First, the sample must contain not more than 12 mg SiO_2 , otherwise the rate of formation of the molybdatosilicic acid complex is altered. Second, the amount of HCl in the initial methanolic solution must be such as to convert the cations present in the silicate into their chlorides and to provide an excess which will make the silicic acid solution about 0.1 M with respect to HCl.

The silicic acid solution must be used immediately for the complexing reaction, which is described later.

Preparing the silicic acid solution of the silicate samples is the point where mistakes are made very easily. Therefore the necessity of very good mixing of the methanolic reagent while the silicate is dissolving must be emphasized. If mixing is inadequate,

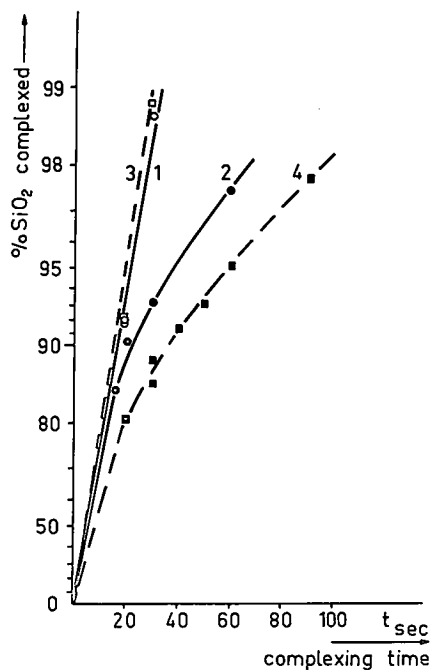


Figure 2. Kinetics of the complexing reaction for Co_2SiO_4 at 20 C. Curve 1—methanolic HCl solution, complexing reagent added after 30 sec; curve 2—methanolic HCl solution, complexing reagent added after 10 min; curve 3—aqueous HCl solution, complexing reagent added after 30 sec; curve 4—aqueous HCl solution, complexing reagent added after 10 min. In all cases the H_4SiO_4 concentration is 0.1 g per 100 ml of solvent.

ened and dispersed with a glass rod to make of 1 N NaOH (5) are then added in order to dissolve the precipitate.

Five drops of the indicator (3) are added and the excess hydroxide back-titrated with 0.5 N HCl (4). The end point is marked by a very sharp change from blue to yellow. The reaction



has been found to occur quantitatively with the indicator specified (7, 8, 9). Therefore each ml of standard 1 N NaOH (reagent 5) that has been used to dissolve the precipitate to form MoO_4^{2-} , and which has therefore not been back-titrated with the 0.5 N HCl, is equivalent to 2.504 mg of complexed SiO_2 . The percentage of SiO_2 complexed in time t is calculated from the ratio of the weight in mg of SiO_2 thus obtained and the total amount in mg of SiO_2 in solution, G_0 .

A number of such estimations are made with different values of the complexing time, t ; usually 3-10 such values are required. The percentages of SiO_2 complexed are plotted on a logarithmic scale against t (see following section). The resulting curve is called the reaction curve (Fig. 1).

the rapid conversion of the silicate to silicic acid is liable to cause the formation of a high local concentration of dissolved silicic acid that will subsequently condense very rapidly, and can lead to serious errors.

Determination of the Reaction Curve

A 40-ml portion of the acidified molybdate solution (7) must be placed in the thermostat at 20 C so that it is already at this temperature at the moment when it is required.

To the beaker containing the methanolic solution of the silicate sample are added 40 ml of solution (7), and a stopwatch is started at this moment. After the desired complexing time, complex formation is stopped by addition of 25 ml of conc HCl (1).

At least 15 seconds after adding the conc HCl, 25 ml of the quinoline solution (2) are added from a burette, causing the yellow quinoline salt $(\text{C}_9\text{H}_7\text{NH})_4(\text{SiMo}_{12}\text{O}_{40})\cdot\text{aq}$ to precipitate. The mixture is then cooled to 10-15 C. The precipitate is filtered in a sintered glass crucible of porosity G4 and carefully washed with cold water until all the HCl has been removed. At the end of this operation the outside of the crucible is also washed free from HCl.

The sintered glass crucible with the precipitate is now placed in a 600-ml beaker and water added until it is just covered. The yellow precipitate is loos-

the subsequent dissolving easier; 10 ml

TABLE 1
HALF-LIFE TIME AND COMPLEXING RATE CONSTANT FOR
SINGLE SILICIC ACIDS

Silicic Acid (1)	Starting Material (2)	Number of Si-O-Si Bonds (3)	Half-Life Time τ Sec (4)	K_n , Sec ⁻¹ (5)
Mono-	Ca ₂ SiO ₄ ^a	0	5.5	0.12
Di-	Ca ₂ Na ₂ Si ₂ O ₇ ^b	1	23.5	0.032
Trimeta-	Ca ₃ Si ₃ O ₉ ^c	3	36	0.019
Tetrameta-	K ₄ H ₄ Si ₄ O ₁₂ ^d	4	83	0.0084
Hexameta-	Cu ₆ Si ₆ O ₁₈ · 6 H ₂ O ^e	6	360	0.0018

^a β - and γ -Ca₂SiO₄ were found to give identical results.

^bBesides Ca₂Na₂Si₂O₇, Ca₃Si₂O₇ (rankinite) was also used; it required a longer solution time and gave complexing rates sometimes lying on a curved line. The curve was in substantial agreement with Ca₂Na₂Si₂O₇ only if the Ca₃Si₂O₇ could be dissolved within 30 sec.

^cFor structure of pseudowollastonite see (11).

^dFor preparation and structure see (12) and (13).

^eSee (16).

RESULTS AND DISCUSSION

Control Solutions Containing Defined, Uniform Silicic Acids and Their Complexing Rates

There is a linear relationship between the logarithm of the concentration of unreacted silicic acid in solution and the reaction time, t . The reaction is therefore first order, and its rate can be expressed as

$$-\frac{dG_t}{dt} = K_n \cdot G_t$$

where G_t is the concentration at time t , and K_n is the reaction rate constant for the specific silicic acid studied. The K_n values may be different if the conditions of the procedure are modified (2, 3, 4, 6).

The methanolic HCl solutions used in the present work were made by dissolving anhydrous HCl gas in pure methanol. Water accelerates the condensation of silicic acids (10) and may thus be expected to retard the formation of the molybdate complex. The complexing rates given in Table 1 are therefore possibly greater than for any other method of preparation of silicic acids described in the literature.

We prepared solutions each containing only one type of silicic acid by dissolving crystalline silicates with known, uniform anions (Table 1, col. 2) in methanolic HCl. That the silicic acids were indeed brought into solution without condensation is shown by the fact that the reaction curves are straight lines. Inadequate stirring during the dissolution or standing of the silicic acid solution before the addition of the complexing reagent yields values which give rise to nonlinear curves. Figure 2 shows reaction curves for H₄SiO₄. A straight line is obtained only when the complexing reagent is added immediately after the sample of Ca₂SiO₄ has been dissolved in methanolic HCl (Fig. 2, curve 1) or in aqueous HCl (curve 3). Ten minutes of standing in methanol at 20 C before the complexing reagent was added yielded curve 2, whereas 10 minutes of standing in water at 20 C yielded curve 4. The greater curvature of this last curve is due to the more rapid condensation of H₄SiO₄ in aqueous solution.

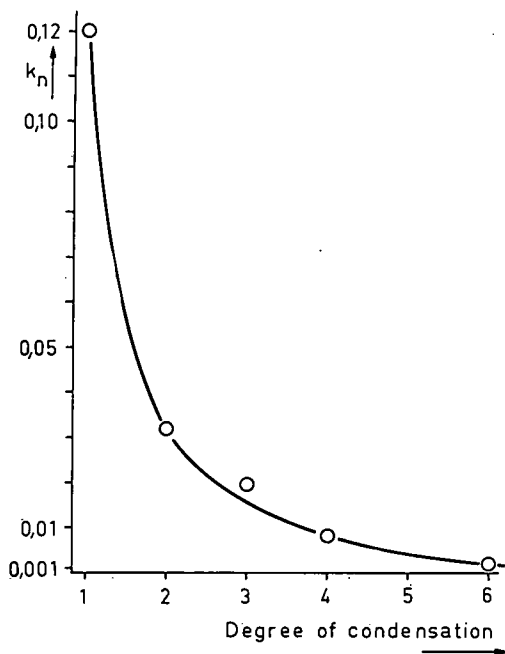


Figure 3. Complexing rate constants K_n of defined and uniform silicic acids plotted against the number of $\text{Si}(\text{O}, \text{OH})_4$ tetrahedra in the anion of the parent silicate.

curves 2 and 4 in Fig. 2). Curve 6 in Figure 1 has the same slope as curve 4, showing that the mixture contained a large proportion of tetrametasilicate. If its upper portion is extrapolated to zero time, it crosses the y-axis at 50 percent. This is to be expected, since 50 percent of the SiO_2 in the original mixture was present as tetrametasilicate.

From the values of K_n listed in Table 1 it is not yet possible to recognize the exact relationship between the complexing rate and the number of Si-O-Si bonds. One could expect to find such a regularity if one was able to compare the results for a number of silicic acids of different chain lengths. Since crystalline silicates with chain anions containing more than 2 tetrahedra are not yet known (except long chains), we are not able to prepare the corresponding silicic acids. The ring-shaped silicic acids with 3, 4 or 6 tetrahedra certainly differ from each other in stability. For silicates with ring anions the complexing rate may well be influenced by strain as well as by the number of Si-O-Si bonds. A certain regularity can nevertheless be seen in Figure 3, in which the values of K_n are plotted against the number of $\text{Si}(\text{O}, \text{OH})_4$ tetrahedra in the silicic acid. This curve could be used to estimate approximately the degree of condensation for silicic acids that are unknown in crystalline silicates.

The value of K_n found for the trimetasilicic acid does not lie on the curve shown in Figure 3. This value was obtained using pseudowollastonite ($\text{Ca}_3\text{Si}_3\text{O}_9$) (11) as starting material. When this silicate is treated with the methanolic HCl, there is usually a residue which remains undissolved even after some minutes. Impurities of more highly condensed silicates, e.g., wollastonite, which has chain-like anions, could not be detected by X-rays. This substance has been dissolved as is described for calcium silicate hydrates in the next section.

The silicates Ca_2SiO_4 , $\text{Ca}_2\text{Na}_2\text{Si}_2\text{O}_7$, and $\text{K}_4\text{H}_4\text{Si}_4\text{O}_{12}$ (12, 13), which were used as standards, dissolve in 10 to 30 sec. However, not all silicates containing isolated SiO_4 tetrahedra or other small anions are soluble in methanolic HCl. Those containing small, highly charged cations (e.g., Mg^{2+} , Zn^{2+} or Al^{3+}) either dissolve very slowly in acids (e.g., willemitte, Zn_2SiO_4 ; forsterite, Mg_2SiO_4 ; grossular, $\text{CaAl}_2(\text{SiO}_4)_3$)

The half-life times τ (Table 1, col. 4) are taken from the reaction curves in Figure 1. The rate constant for each silicic acid (col. 5) is calculated by using the relationship

$$K_n = \frac{0.693}{\tau}$$

The reaction curves for the control solutions containing known and uniform silicic acids showed that:

1. Under the conditions used, H_4SiO_4 reacts more quickly than any of the condensed silicic acids.
2. The speed of hydrolytic degradation of a condensed silicic acid depends on its degree of condensation.
3. The complexing rate (expressed either by K_n or by the half-life time τ) has a characteristic value for each silicic acid and thus allows their identification; this cannot be generalized, however, to the corresponding anions in solid silicates.
4. The complexing rate follows approximately a first-order law. On a logarithmic scale the reaction curve for a uniform silicic acid is a straight line; mixtures give nonlinear curves (curve 6 in Fig. 1;

curve 6 in Figure 1 has the same slope as curve 4, showing that the mixture contained a large proportion of tetrametasilicate. If its upper portion is extrapolated to zero time, it crosses the y-axis at 50 percent. This is to be expected, since 50 percent of the SiO_2 in the original mixture was present as tetrametasilicate.

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or are insoluble (pyrope, $Mg_3Al_2(SiO_4)_3$; zunyite, $Al_{13}Si_5O_{20}(OH)_{18}Cl$). Some others, such as diopside ($Cu_6Si_6O_{18} \cdot 6 H_2O$), are only soluble in methanolic HCl if the concentration exceeds 0.5 M.

Study of Changes in the Degree of Anion Condensation in Calcium Silicate Hydrates

In calcium silicate hydrate gels and similar materials, the anions in a single preparation vary over a range of sizes, the distribution of which is too complex for analysis by the method described earlier. Moreover, they may contain a proportion of highly condensed anions, and thus be incompletely soluble in the methanolic HCl. The method can, however, be modified so as to provide comparative information on such preparations: Such comparative information can be used, for instance, in studies of the changes in the distribution of anion sizes brought about by hydrothermal or other modes of treatment.

For slowly soluble silicates no general procedure can be given at the moment because a number of possible errors can arise during the solution of such substances. To study calcium silicate hydrates we avoid these errors by dissolving the sample first in methanolic HCl, separating all the material which does not dissolve within one minute. The amounts of SiO_2 contained in the more highly condensed silicates in the residue are estimated directly.

The soluble silicates are estimated in a new sample of a weight calculated on the basis of the insoluble part. It is also necessary to calculate the amount of silicate that must be used to give about 25 mg SiO_2 in 25 ml of methanolic HCl. This must contain 0.68 g HCl per 100 ml methanol. The silicate sample is well shaken with the methanolic HCl and filtered after 20 sec through a sintered glass crucible of porosity G3. Two 10-ml aliquots are taken. One of these is used immediately for the complexing reaction, which is carried out in a normal way as described earlier. The other is used to determine the weight of SiO_2 dissolved, G_0 .

For the G_0 estimation, the 10-ml aliquot is mixed with 40 ml of the complexing reagent (7) and this mixture is heated at near the boiling point for about one hr. It is then allowed to stand for about 15 hr at room temperature and the procedure described earlier is then followed.

We have observed that tobermorite-like calcium silicate hydrates (C-S-H(I) and C-S-H(II) in particular) dissolve within 30 sec if they have a lower degree of condensation, thus giving reliable results. For such comparative estimations of the type under discussion it is sufficient to use a mixture of methanol with conc aqueous HCl. To dissolve, for example, 28.7 mg of Ca_2SiO_4 (containing 10 mg SiO_2), 9 ml of a methanolic solution that contains 0.68 g HCl in 100 ml, i.e., 1.6 ml of aqueous HCl ($d = 1.81$), are needed. Over a third of this solution by weight is HCl, and the methanolic solution therefore contains about 1 percent water.

If the sample is dissolved directly in the aqueous molybdic acid solution, pure silicates may be distinguished "if they are dissolved in a very short time" (6). However, with some monosilicates the time required to effect solution exceeds the time which is needed to form the molybdate complex from even a highly condensed silicic acid. Methods in which the silicate is treated directly with the aqueous molybdic acid solution therefore do not appear suitable for the analysis of materials containing a range of anion sizes (e.g., calcium silicate hydrate gels), because it is not possible to distinguish the effect of slow dissolution from that of the slow complexing reaction of a highly condensed silicic acid.

The use of methanolic HCl for extraction offers some advantages over the use of aqueous HCl:

1. H_4SiO_4 is much more soluble in methanolic HCl than in aqueous HCl (14, 15) but condensation is much slower in methanol than in water (10). This can reduce errors.
2. Better separation of the highly condensed silicates is achieved with methanol. Water degrades slowly even the highly condensed and therefore insoluble silicic acids. By hydrolysis of Si-O-Si bonds on the surface, a small amount of H_4SiO_4 is formed which dissolves readily. With acidified molybdate solution the complexing rate of undissolved silicates with long chain anions is retarded about 30 times compared with

silicic acids in solution and in case of sheets about 500 times. Even quartz powder yields the complex very slowly. Such hydrolysis does not occur in methanolic HCl even if it contains about 5 percent water.

3. The slow condensation of silicic acids enables the analysis of mixtures in favorable cases (e.g., Fig. 1, curve 6) or gives information on the distribution of anion sizes in the material that has gone into solution.

This modified method is especially suitable for investigating changes in anion sizes by comparing the reaction curves of samples.

It should be noted that carbonated preparations containing CaCO_3 yield an equivalent amount of silicic acid in a highly condensed state which will dissolve neither in methanol nor in water.

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